

Determination of trace metals in natural samples by ICP-OES after preconcentration on modified silica gel and on modified silica nanoparticles

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Abstract Silica gel and nanometer SiO₂ modified with 4-(2-aminoethylamino)-*N*-(2-(2-aminoethyl amino)ethyl) butanamide (SG-AAEB and nanometer SiO₂-AAEB), which were prepared based on chemical immobilization, were used as sorbents for the solid phase extraction of Cu(II), Fe(III), and Pb(II) prior to their determination by inductively coupled plasma optical emission spectrometry. Adsorption efficiencies of the two sorbents towards metal ions were investigated by batch and column procedures. For both sorbents the preconcentration conditions of analytes including effects of pH, shaking time, sample flow rate and adsorption capacity, were investigated and compared. The differences of silica gel and nanometer SiO₂ in sizes and surface structures resulted in distinct chemical activity and selectivity toward metals. At pH 4, the adsorption capacity of SG-AAEB was found to be 12.2, 14.5 and 9.8 mg g⁻¹ for Cu(II), Fe(III), and Pb(II), respectively. In comparison, nanometer SiO₂-AAEB showed a high selectivity toward Pb(II) and has a much larger adsorption capacity (22.3 mg g⁻¹). Furthermore, the

application of SG-AAEB and nanometer SiO₂-AAEB for simultaneous preconcentration of trace Cu(II), Fe(III), and Pb(II) from natural samples was performed with satisfactory results.

Keywords Silica gel · Nanometer SiO₂ · Amide modification · Trace metals · ICP-OES · 4-(2-aminoethylamino)-*N*-(2-(2-aminoethylamino) ethyl) butanamide

Introduction

Determination of trace metals in natural samples by ICP-OES after preconcentration on modified silica gel and on modified silica nanoparticles. The determination of trace heavy metal ions in environmental samples has received increasing attention [1–3]. However, the direct determination of metal ions at trace levels is limited due to their low concentrations and matrix interferences. Therefore, the preconcentration and determination of trace metals in real samples have been a topic of interest in environmental evaluation and protection study.

One of widely used and fast emerging preconcentrative separation techniques is the solid-phase extraction (SPE). It has been known as a powerful tool for separation and enrichment of various inorganic and organic analytes [4]. The major advantages of SPE include: (i) higher enrichment factor, (ii) absence of emulsion, (iii) safety with respect to hazardous samples, (iv) ease of automation, (v) minimal costs due to low consumption of reagents, (vi) the ability to combine with different modern detection techniques [5, 6]. Nevertheless, the lack of selectivity is a main

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drawback of SPE [7], which leads to high interference of the other existing species with the target metal ion. Selectivity of the solid phase extractors mainly depends on the structure of the immobilized organic compound as a whole, the nature of the incorporated donor atoms (O, N, P and S), the positioning of the functional groups along the surface of the solid support and the steric requirements of the complex formed after uptake of the desired metal ion [8]. Based on this, the chemical or physical modification of the sorbent surface with some organic compound is usually used to increase the selectivity by loading the surface with some donor atoms such as oxygen, nitrogen, sulfur and phosphorus.

Among many types of solid phase extractors, silica gel presents the advantages of no swelling, fast kinetics, good mechanical as well as the thermal and chemical stability [9, 10]. Chemical modification of silica surface by immobilization of functional groups has been reported for extractive concentration of metal ions [11, 12]. In addition, nanometer material, a new solid material, is currently becoming more important due to its special physical and chemical properties. One of nanoparticle's properties is that most of the atoms are on the surface. The surface atoms are unsaturated and therefore can bind with other atoms that possess highly chemical activity. Consequently, nanometer material can selectively adsorb metal ions, and presents a very high adsorption capacity [13]. Investigations of the surface chemistry of highly dispersed oxides, e.g. SiO₂, TiO₂, Al₂O₃, ZrO₂, CeO₂ and ZnO, show that these materials have a very high sorptive capacity [14–16] and give promising results when used for trace-metal analyses of different types of water [17, 18] and solutions of high-purity alkali salts [19]. Nanometer SiO₂ is a promising material as a solid-phase extractant because of its large specific surface area, high adsorption capacity and low temperature modification. It has been widely used to prepare complex materials and as carrier of catalyst [20]. Recently, organic groups modified nanometer SiO₂ have been reported for the separation and preconcentration of metal ions in biological and environmental samples [21, 22].

Silica gel and nanometer SiO₂ have the same composition (silicon and oxygen), and there are several reports on the use of functionalized nanometer SiO₂ and silica gel for metal enrichment. However, less attention has been devoted to the differences between silica gel and nanometer SiO₂ based sorbents. Therefore, the different adsorption behaviors of the nanometer SiO₂ and silica gel based solid phase extractants were focused on in this study. 4-(2-Aminoethylamino)-*N*-(2-(2-aminoethylamino)ethyl)butanamide (AAEB) modified silica gel and nanometer SiO₂ were synthesized and characterized. The preconcentration conditions of two analytes were investigated, compared and analyzed, including effects

of pH, shaking time, the sample flow rate and adsorption capacity. Nanometer SiO₂ modified with AAEB (nanometer SiO₂-AAEB) showed greater affinity and higher adsorption capacity for binding with Pb(II) than that of silica gel modified with AAEB (SG-AAEB). In addition, satisfied results were achieved when the two sorbents were applied to the determination of trace Cu(II), Fe(III), and Pb(II) in natural samples.

Experimental

Apparatus

An IRIS Advantage ER/S inductively coupled with plasma spectrometer (TJA, USA, www.thermo.com) was used for all metal-determinations. The operation conditions and the wavelengths were summarized in Table S1 (Electronic Supplementary Material).

The pH values were controlled with a pHs-10C digital pH meter (Xiaoshan Instrument Factory, China, www.cntr.com). Infrared spectra were recorded on a Nicolet NEXUS 670 FT-IR apparatus (U.S.A, www.thermo.com) using KBr pellet.

A YL-110 peristaltic pump (The general research academe of colored metal, Beijing, China, www.grimm.com) was used in the separation/preconcentration process. A PTFE (polytetrafluoroethylene) column (45 mm × 3.0 mm i.d.) was used in this study.

Reagents and standard solutions

Unless otherwise stated, all reagents used here were of analytical grade and all solutions were prepared with doubly distilled deionized water. Diethylenetriamine (DETA) and chloroacetyl chloride were used in this work (The First Reagent Factory, Shanghai, China, www.reagent.com). 3-Chloropropyltrimethoxysilane (CPS) was purchased from Chemical Engineering Corporation of Ocean University of China (Qingdao, China, www.quxing.com). Nanometer SiO₂ was synthesized according to the method reported [23, 24] (The average diameter is 60–80 nm).

Standard stock solution of Cu(II), Fe(III), and Pb(II) (1 mg mL⁻¹) were prepared by dissolving spectral pure chemicals and made up in 1 mol L⁻¹ nitric acid. Standard stock solutions of other ions (1 mg mL⁻¹) were prepared according to standard method and further diluting daily prior to use as well. The preparations of natural samples were shown in Supplementary Information. HCl (pH 1.0–2.0), acetate–acetic acid buffer (pH 3.0–5.0), phosphate buffer (pH 6.0–7.0), NH₃–NH₄Cl buffer (pH 8.0–10.0) were used for pH adjustment.

Modification process

Synthesis of chloro-functionalized silica gel and nanometer SiO₂ sorbents

Silica gel and nanometer SiO₂ were activated with hydrochloric acid as described previously [25], respectively. Activated silica gel (10 g) or nanometer SiO₂ (5 g) was dispersed into 100 mL toluene in a 250 mL three-necked flask equipped with a refluxing condenser, a thermometer and an agitator. Then 3-chloropropyltrimethoxysilane (10 mL) was gradually added with continuously stirring. The mixture was refluxed for 6 h, filtered off, washed with toluene and ethanol and dried at 60 °C for 6 h. The product was silica gel or nanometer SiO₂ bound 3-chloropropyl phase (SGBCP or nanometer SiO₂-BCP).

Synthesis of SG-AAEB and nanometer SiO₂-AAEB

SGBCP (10 g) or nanometer SiO₂-BCP (5 g) was suspended in 75 mL of dry toluene. The mixture was stirred and refluxed for 12 h after adding to 16 mL of diethylenetriamine. The solvent was filtered off, washed with toluene, ethanol and diethyl ether and dried in an oven at 60 °C for 8 h. The product was transferred into the flask, and then 100 mL of dried ethanol was added followed by 2.5 mL chloroacetyl chloride. The reaction mixture was stirred for 4 h at 0–5 °C under nitrogen atmosphere, filtered under vacuum, washed with ethanol and dried under vacuum at 60 °C for 6 h. Finally, the product was suspended in 75 mL of dry toluene, and 10 mL of diethylenetriamine were added to the suspension and refluxed for 12 h to obtain silica gel or nanometer-SiO₂ modified with 4-(2-aminoethylamino)-*N*-(2-(2-aminoethyl amino)ethyl)butanamide (SG-AAEB or nanometer SiO₂-AAEB). The synthetic route of SG-AAEB was illustrated in Fig. 1.

Procedures

Adsorption efficiencies of the two sorbents toward metal ions were investigated by the batch and column procedures (listed in Supplementary Information), respectively.

Results and discussion

FTIR spectra

The modified silica gel was confirmed by IR analysis. IR absorption spectrum of chloro-functionalized silica gel shows the appearance of bands at 468.90, 806.46, 1100.59, 1639.17, 2926.85 and 3433.94 cm⁻¹, due to

δ(Si-O-Si), ν(Si-O-Si), longitudinal SiO₂ lattice vibration, δ(H₂O), ν(CH₃) and ν(Si-OH) [26], respectively.

Comparing the IR spectrum of SG-AAEB and SGBCP, we found the new bands that appeared at 1594.63, 1513.45, 1484.51, 1390.82, 1349.10, 1315.05 cm⁻¹. The bands around 1513.45 and 1594.63 cm⁻¹ were assigned to ν(C=O) and δ(N-H) in the SG-AAEB. The peak at 1315.05 cm⁻¹ is C-N stretching vibration. The peak at 1,390.82 cm⁻¹ is due to CH₂ shear deformation vibration. SG-AAEB and nanometer SiO₂-AAEB showed a similar location and appearance of the major bands, indicating the successful modifications of silica gel and nanometer SiO₂ with 4-(2-aminoethylamino)-*N*-(2-(2-aminoethyl amino)ethyl)butanamide [27].

Effect of the pH on enrichment recovery

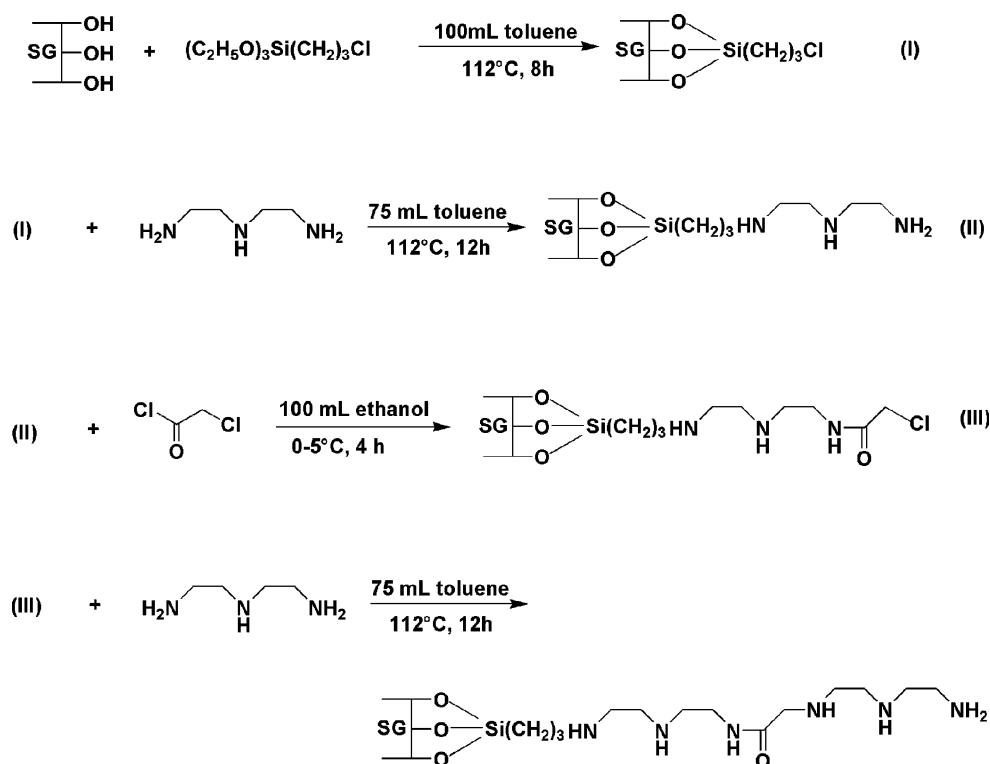
Solution acidity has two effects on metal adsorption: proton in acid solution can protonate binding sites of the chelating molecules, and hydroxide in basic solution may complex and precipitate many metals. Therefore, pH value is the first parameter to be optimized.

The adsorption of SG-AAEB and nanometer SiO₂-AAEB toward thirteen metal ions, namely Mg(II), Ca(II), Cr(III), Mn(II), K(I), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II), were tested at different pH values (pH 1 to 7) following the batch procedure, respectively.

The results showed that the highest metal recovery values (listed in Fig. 2) were found for simultaneous preconcentration of Cu(II), Fe(III), Pb(II) by SG-AAEB at pH ranging from 4 to 7. As seen from Fig. 2, only Pb(II) could be quantitatively adsorbed on the nanometer SiO₂-AAEB at pH ranging from 2 to 7, and other metal ions had an insignificant adsorption on the nanometer SiO₂-AAEB. Evidently, nanometer SiO₂-AAEB showed a higher selectivity toward Pb(II) than SG-AAEB.

Four possible factors may be responsible for this result. The first is the nature, charge, and size of the metal ions [28]. Second, AAEB is a chain compound contained donor atoms (N, O). When immobilized on a suitable support material, it had a tendency to form metal complexes with certain metal ions in solution. The third is the quality of the solid support. The differences in size, surface structure and inter-particle interaction of silica gel and nanometer SiO₂ lead to their distinct chemical activity and selectivity [7]. The fourth is OH—on the surface of the adsorbents. At high pH, the OH—on the surface provides the ability of binding cations. The decrease of pH leads to the neutralization of surface charge, and OH— is displaced from the surface, so the adsorption of cations onto adsorbents decreases quickly. In addition, nanometer SiO₂ has a fine grain size and high surface area. It may be the another reason for the high selectivity of nanometer SiO₂-AAEB toward Pb(II). To avoid hydrolyzing at higher pH, pH4 was

Fig. 1 Synthetic route of the SG-AAEB



selected as the enrichment acidities of SG-AAEB and nanometer SiO_2 -AAEB for further study.

Influence of elution condition on recovery

Figure 2 also showed that the adsorption of cations at $\text{pH} < 2$ is negligible, one can expect that elution may be favored in acidic solution. So various concentrations and volumes of HNO_3 were used for desorption of the studied ions following the column procedure. The obtained results over SG-AAEB were shown in Table 1. The quantitative recoveries ($> 95\%$) could be obtained using 4 mL of 0.5 mol L^{-1} HNO_3 as eluent. In addition, similar results

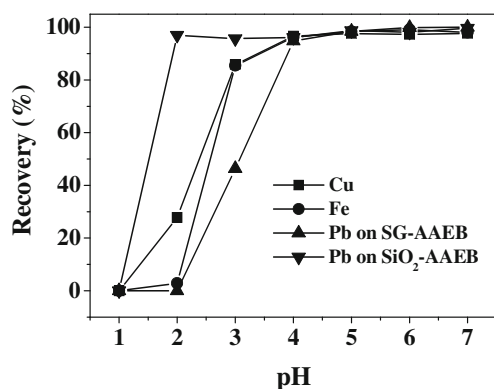


Fig. 2 Effect of pH on analytes recovery over SG-AAEB (10 mL of $1.0\text{ }\mu\text{g mL}^{-1}$ $\text{Cu}(\text{II})$, $\text{Fe}(\text{III})$ and $\text{Pb}(\text{II})$) and nanometer SiO_2 -AAEB ($1.0\text{ }\mu\text{g mL}^{-1}$ $\text{Pb}(\text{II})$); sample mass: 35 mg , shaking time: 30 min , temperature 25°C

were also obtained over nanometer SiO_2 -AAEB. Therefore, 4 mL of 0.5 mol L^{-1} HNO_3 was used as eluent in subsequent experiments.

Effect of extractant mass

To test the effect of extractant mass on quantitative retention of analytes, different amounts of SG-AAEB and nanometer SiO_2 -AAEB (range from 5 to 40 mg) were added into the solution following the batch procedure, respectively. The results were shown in Fig. 3. Quantitative recoveries ($> 95\%$) for the examined analytes were obtained in range of 30 – 40 mg of two sorbents. Quantitative retention was not obtained when amounts of extractors were less than 30 mg . So 35 mg of SG-AAEB and nanometer SiO_2 -AAEB were selected for further study.

Effect of shaking time

The effect of shaking time on the percentage extraction of metal ions is considered to be of significant importance to determine the possible discrimination order in the behaviour of the new synthesized phases towards the different metal ions [29]. This factor is studied to determine the equilibration rate and flow rate for further study. Different shaking time (range from 2 to 30 min) was studied for the percentage extraction of metal ions. It was found that only 2 min was needed for maximum recovery ($> 95\%$), which indicated that SG-AAEB had rapid adsorption kinetics for

Table 1 Elution recovery (%) for Cu(II), Fe(III), Pb(II) adsorbed on SG-AAEB

Concentration (molL ⁻¹) ^a	0.01	0.05	0.1	0.5	1	2
Cu(II)	46.9	72.3	97.1	98.3	100	100
Fe(III)	51.4	86.9	89.8	96.8	100	100
Pb(II)	46.5	67.3	92.7	95.9	98.7	97.6
Eluent volume (mL) ^b	2	3	4	5	6	8
Cu(II)	53.6	82.8	95.7	98.0	100	100
Fe(III)	64.9	89.3	97.6	100	100	100
Pb(II)	68.0	90.4	97.1	99.8	100	100

^a 10 mL HNO₃^b 0.5 mol L⁻¹ HNO₃

simultaneous preconcentration of Cu(II), Fe(III) and Pb(II). However, the percentage extractions of Pb(II) on nanometer SiO₂-AAEB reach the maximum recovery at 20 min. So 20 min was needed to reach equilibrium for the adsorption of Pb(II). The lower dispersion of nanometer SiO₂-AAEB sorbent in the solution might lead to the longer shaking time to reach maximum recovery.

Effect of the flow rate

The flow rate of the sample solution through the packed volume is a very important parameter because the retention of elements on sorbent depends upon the flow rate of the sample solution.

SG-AAEB and nanometer SiO₂-AAEB were applied in the SPE column, respectively. The influences of the flow rate on retention of the studied ions were investigated under the optimum conditions. The flow rates were adjusted in the range of 0.5–3.0 mL min⁻¹. It was found that the retention of Cu(II), Fe(III) and Pb(II) on SG-AAEB sorbent were practically not changed up to the flow rate of 1.5 mL min⁻¹. And the recoveries of the analytes decreased significant when the flow rate was over 1.5 mL min⁻¹. Thus, a flow rate of 1.5 mL min⁻¹ was employed for SG-AAEB sorbent.

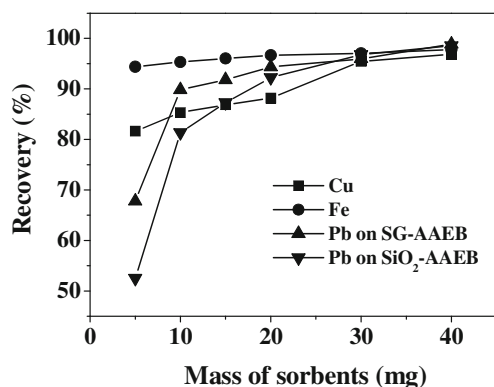


Fig. 3 Effect of extractant mass on analytes recovery over SG-AAEB (10 mL of 1.0 μg mL⁻¹ Cu(II), Fe(III) and Pb(II)) and nanometer SiO₂-AAEB (1.0 μg mL⁻¹ Pb(II)); pH: 4, shaking time: 30 min, temperature: 25 °C

The results also indicated that quantitative recovery of Pb (II) could be achieved on nanometer SiO₂-AAEB sorbent at flow rates lower than 1.5 mL min⁻¹. The reason might be that high flow rates were limited by the backpressure, resulted from the fine grain size of the nanometer material. Nevertheless, low flow rates decreased the sample throughput, resulting in a long time of analysis. Based on these, a flow rate of 1.0 mL min⁻¹ was selected for nanometer SiO₂-AAEB.

Effect of sample volume and preconcentration factor

In order to explore the possibility of concentrating low concentrations of analytes from large volumes of solution, the effects of sample volume on the retention of metal ions were also investigated. For this purpose, 20–400 mL of sample solutions containing 1.0 μg of Cu(II), Fe(III) and Pb(II) were passed through the microcolumn at the optimum flow rate. Quantitative recoveries (>90%) were obtained for sample volumes of ≤300 mL for Cu(II), ≤200 mL for Fe(III) and ≤200 mL for Pb(II), respectively. Under the same experiment, the maximum sample volume of nanometer SiO₂-AAEB could be up to 300 mL with the recovery >90%. Therefore, the preconcentration factors were Cu(II): 75, Fe(III): 50 and Pb(II): 50 for SG-AAEB and Pb(II): 75 for nanometer SiO₂-AAEB, respectively, since the final elution volume was 4 mL.

Effects of matrix ions

The effects of common coexisting ions on the adsorption of studied ions on SG-AAEB and nanometer SiO₂-AAEB were investigated, respectively. In these experiments, different foreign ions were added to equal quantities of the diluted mixed standard solutions and enriched and determined according to the general procedure. The results showed that in excess of 1,000 μg mL⁻¹ of K(I), Na(I) and Mg(II), 50 μg mL⁻¹ of Ca(II), 20 μg mL⁻¹ of Ni(II), Zn(II), Co(II), Cd(II) and Cr(III), 2 μg mL⁻¹ of Mn(II) had insignificant interferences with the determination of the analytes. The possible factor for this reason is the amino-functionalized group inherent selectivity. The amino group

is a soft base and it would not interact with alkali metal and alkali earth metal ions that are classified as hard acids [21].

Stability tests

To test the stability, both of sorbent materials were subjected to several loading and elution bath operations. The adsorption conditions were referenced according to the above experiments. The elution operations were carried out by shaking the sorbents with 20 mL of 0.5 mol L⁻¹ HNO₃ for 2 h in order to ensure complete equilibration. Then the sorbents were treated with doubly distilled deionized water until neutral equilibration was reached. The operating capacities were calculated from the loading and elution tests. The results from three tests yielded <5% error up to 15 cycles of repeated experiments. Both of sorbents showed better reusability and stability towards the studied metal ions.

Adsorption capacity

The adsorption capacity is an important factor because it reflects how much sorbent is required to quantitatively concentrate the analytes from a given solution. The capacity study was adopted from the paper recommended by Maquieira et al. [30]. According to the batch procedure, 10 mL aliquots of a series of concentrations (10–100 mg L⁻¹) were adjusted to the appropriate pH. A breakthrough curve (listed in Fig. 4) was gained by plotting the concentration (mg L⁻¹) vs. micrograms of metal ions adsorbed per gram. From the breakthrough curve, the adsorption of SG-AAEB for simultaneous preconcentration of Cu(II), Fe(III), and Pb(II) was found to be 12.2, 14.5 and 9.8 mg g⁻¹, respectively. The adsorption capacity of nanometer SiO₂-AAEB for Pb(II) was 22.3 mg g⁻¹. Obviously, nanometer SiO₂-AAEB had a much higher adsorp-

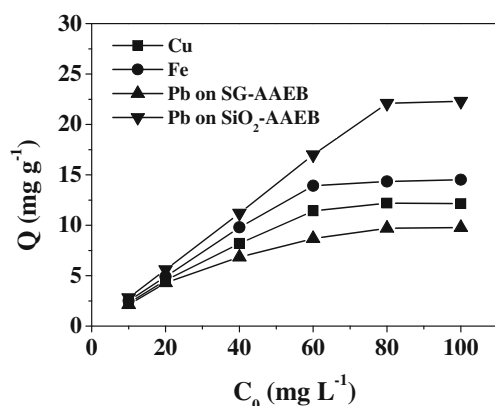


Fig. 4 Adsorption capacity of Cu(II), Fe(III) and Pb(II) on on SG-AAEB and nanometer SiO₂-AAEB sorbents; pH: 4; Sample volume: 10 mL

Table 2 Analysis results for the determination of trace metals on SG-AAEB and nanometer SiO₂-AAEB sorbents in standard reference material (GBW 08301, river sediment)

Element	Found (μg g ⁻¹)	Certified (μg g ⁻¹)
Cu	51±3.0	53±6.0
Fe	39,380±120	39,400±1,300
Pb	76±3.0	79±12.0
Pb ^a	77±1.0	79±12.0

The value following “±” is the standard deviation (*n*=3)

^a Analysis results for the determination of Pb on nanometer SiO₂-AAEB sorbent in standard reference material

tion capacity for Pb(II), which was related to the special properties of nanometer material as ultrafine grained particle [31].

Moreover, the adsorption capacity of nanometer adsorbent for metal ions in some other reports (Cu: 6.2 mg g⁻¹ [30]; Fe: 4.7 mg g⁻¹ [20]; Pb: 19 mg g⁻¹ [32] and 15.4 mg g⁻¹ [16]) was lower than that of two sorbents. The difference resulted from the different size of the solid support and the chelate compound.

Analytical precision and detection limit

Under the selected conditions, eight portions of mixed standard solutions were enriched and analyzed simultaneously by following the batch procedure. SG-AAEB and nanometer SiO₂-AAEB sorbents were investigated, respectively. The results showed that the relative standard deviations (RSDs) of the method were lower than 3.5% (Cu(II): 1.95%; Fe(III): 1.64%; Pb(II): 3.47%). According to the definition of IUPAC, the detection limits (3σ) of this method for Cu(II), Fe(III) and Pb(II) were 0.77, 0.51 and 1.23 ng mL⁻¹, respectively. For nanometer SiO₂-AAEB sorbent, the RSDs are 1.02%, and the 3σ for Pb(II) was 0.35 ng mL⁻¹. These results indicate that the method has good precision for the analysis of trace Cu(II), Fe(III) and Pb(II) ions from solution samples.

Table 3 Analysis results for the determination of trace metals on SG-AAEB and nanometer SiO₂-AAEB sorbents in kaolin ore samples

Ion	Found by the suggested method (μg g ⁻¹)	Found by ET-AAS method (μg g ⁻¹)
Cu(II)	0.19±0.07	0.23±0.02
Fe(III)	1.61±0.09	1.72±0.17
Pb(II)	0.22±0.10	0.33±0.05
Pb(II) ^a	0.24±0.08	0.33±0.05

^a Analysis results for the determination of Pb(II) on nanometer SiO₂-AAEB sorbent in kaolin ore samples

Table 4 Analysis results for the determination of trace metals on SG-AAEB and nanometer SiO₂-AAEB sorbents in natural water samples

Ion	Added (μgL^{-1})	Found ^a (μgL^{-1})	Recovery (%)
Yellow River water			
Cu(II)	0	53.75±0.12	96.1
	10	63.36±0.14	
Fe(III)	0	62.25±0.10	97.7
	10	72.02±0.12	
Pb(II)	0	5.02±0.10	95.0
	10	14.52±0.08	
Pb(II) ^b	0	5.02±0.10	99.8
	10	15.00±0.12	
Top water			
Cu(II)	0	5.42±0.13	100.4
	10	15.46±0.10	
Fe(III)	0	9.43±0.11	99.9
	10	19.41±0.17	
Pb(II)	0	2.30±0.09	104.3
	10	12.73±0.08	
Pb(II) ^b	0	2.30±0.10	100.1
	10	12.31±0.07	

^a The value following “ ± ” is the standard deviation ($n=3$)

^b Analysis results for the determination of Pb(II) on nanometer SiO₂-AAEB sorbent in natural water sample

Application of the method

In order to ascertain the accuracy of the suggested procedure, the method was applied to the determinations of trace Cu(II), Fe(III), and Pb(II) in the certified reference material (GBW 08301, river sediment), kaolin ore and nature water samples. SG-AAEB and nanometer SiO₂-AAEB sorbents were applied in the experiment. The analytical results for the standard material (listed in Table 2) were in agreement with the certified values. The analytical results for kaolin ore were listed in Table 3, which were in good agreement with the electrothermal atomic absorption spectrometry (ETAAS) method [33]. For the analysis of natural water samples, the standard addition method was used. The results listed in Table 4 showed that the recoveries were reasonable for trace analysis in range of 95.0–104.3%, which also indicated the reliability of present method.

Comparison with other methods

Table 5 showed the comparison of the suggested method with other SPE methods reported in the literature. Higher sorption capacities, high acidity and low detection limits are some of the advantages of the method. Furthermore, the two adsorbents were synthesized from simple chemicals such as diethylenetriamine and chloroacetyl chloride. There-

Table 5 Figures of merit of comparable methods for determination of Cu(II), Fe(III), Pb(II) by solid-phase extraction

Methods/ reagent(s) used	Analyte	pH	Capacity (mgg ⁻¹)	LOD (ngmL ⁻¹)	PF	Ref.
Silica gel/zirconium phosphate	Cu(II)	4.5		1.1	30	[34]
	Pb(II)	4.5		6.1	30	
Silica gel/nanometer titanium dioxide	Pb(II)	4–7	3.16	9.5	50	[35]
Nanometer SiO ₂ /	Cu(II)	4.0	18.6	1.27		[20]
p-dimethylaminobenzaldehyde	Fe(III)	4.0	4.7	0.40		
	Pb(II)	4.0	6.0	1.79		
Amberlite XAD-7 / xylenol orange	Pb(II)	5.0	3.14		100	[36]
Amberlite XAD-2 / thiosalicylic acid	Pb(II)	4.0	18.44	4.87	100	[36]
Activated Carbon/ phenylpiperazine dithiocarbamate	Cu(II)	4–7		15	400	[37]
	Pb(II)	4–7		57	400	
Activatedcarbon/ 4,6-dihydroxy-2-mercaptopyrimidine	Cu(II)	6.0	0.63	2.9	260	[38]
Nanometer sized alumina/chromotropic acid	Pb(II)	6.0	0.45	8.4	260	
	Cu(II)	7.0–9.0	14.5	0.22	100	[16]
Silica gel/AAEB	Fe(III)	6.0–9.0	16.4	0.54	100	
	Pb(II)	7.0–9.0	15.4	0.53	50	
	Cu(II)	4	12.2	0.77	75	This work
Nanometer SiO ₂ /AAEB	Fe(III)	4	14.5	0.51	50	
	Pb(II)	4	9.8	1.23	50	
	Pb(II)	4	22.3	0.35	75	

fore, the costs of the adsorbents are much less expensive than the commercially available sorbents.

Conclusions

SG-AAEB and nanometer SiO₂-AAEB have been successfully synthesized and applied to solid-phase extraction and preconcentration of Cu(II), Fe(III), and Pb(II) prior to their determination by ICP-OES. The experimental conditions for the preconcentration processes were investigated, compared and analyzed over the two sorbents in detail. The differences of silica gel and nanometer SiO₂ in sizes and surface structures resulted in distinct chemical activity and selectivity toward metals. Nanometer SiO₂-AAEB showed greater affinity, higher selectivity and higher adsorption capacity toward Pb(II) than SG-AAEB, which exhibited highly chemical activity of nanometer material. In addition, the preparations of two sorbents are relatively simple and rapid. The new developed method has been successfully applied to analyze of trace Cu(II), Fe(III), and Pb(II) in kaolin ore and natural water samples.

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